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Comparison of the Reactivity of the Low Buried-Volume Carbene Complexes (ITMe)$_2$Pd(PhC≡CPh) and (ITMe)$_2$Pd(PhN═NPh)

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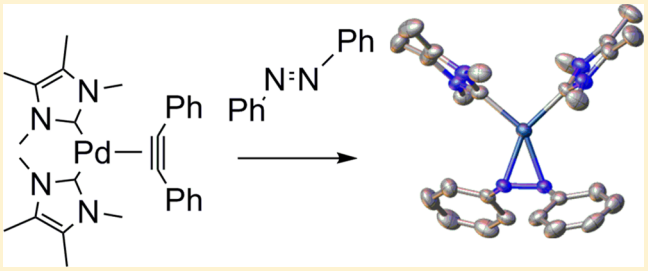
Supporting Information

ABSTRACT: The novel Pd(0)-azobenzene complex (ITMe)$_2$Pd(PhN═NPh) (**5**) (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) has been isolated and characterized in the solid state and by cyclic voltammetry. Its reactivity toward E−E′ bonds (E, E′ = Si, B, Ge) has been compared with that of the known carbene complex (ITMe)$_2$Pd(PhC≡CPh) (**2**). Whereas **2** reacts with all E−E′ bonds studied, **5** only reacted with B−B and B−Si moieties, echoing our previous catalytic studies on azobenzenes.



INTRODUCTION

(NHC)-containing palladium complexes (NHC = *N*-heterocyclic carbene) are very well-documented in the scientific literature. Dominated by bulky ligands, these complexes display tremendous versatility in high turnover number (TON) catalytic reactions.[1−4] Recent reports from our groups have focused on the much smaller carbene ITMe (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene), and its low percentage buried volume Pd(0) complex Pd(ITMe)$_2$ (**1**), as well as the isolable alkyne-bearing complex (ITMe)$_2$Pd(PhC≡CPh) (**2**).[5−7] Both can easily cleave nonactivated E−E′ bonds (E, E′= Si, B), resulting in Pd(II) complexes that can undergo an atom-economical, *Z*-selective addition to internal alkynes affording disilylated or silaborated alkenes. These studies have been underpinned by X-ray structural determinations of potential intermediates and mechanistic studies. Complex **2** and its oxidative addition products **3** and **4** (Scheme 1) are involved in stoichiometric reactions of Si−Si, Si−B, and B−B bonds. Catalytic reactions under mild conditions using very low loadings of **1** or **2** include silaborations, disilylations, and diborations of alkynes and silaborations and diborations of azobenzenes.[8]

These encouraging findings have led us to further explore the scope and reactivity of **2**. First, we wished to explore the synthesis of NHC-containing azobenzene complexes related to **2** to shed some light on the aforementioned catalytic additions of E−E′ bonds to azobenzenes. Next, given our success in achieving low catalyst loadings and mild conditions in a number of E−E′ additions to alkynes, we wished to investigate the use of complexes such as **2** in the activation of Ge−Ge bonds.[9]

RESULTS AND DISCUSSION

We decided to exploit the lability of the alkyne ligand exchange in **2**. The new complex (ITMe)$_2$Pd(PhN═NPh), **5**, was easily synthesized from **2** in the presence of azobenzene and at room temperature (Scheme 2, a). Alternatively, complex **5** could also be prepared directly from the Pd(II)-allyl precursor **6** in a two-step, one-pot procedure in a slightly higher yield (Scheme 2, b).

The ^{1}H NMR spectrum of **5** in C_6D_6 shows clear upfield shifts in the resonances for the N-(1,3)-methyl protons, from 3.49 ppm in **2** vs 3.31 ppm in **5**, and for the C-(4,5)-methyl protons, from 1.54 ppm in **2** vs 1.38 ppm in **5** (see the Supporting Information). In the same way, the ^{13}C{^{1}H} NMR resonance for the carbenic carbon in **5** is significantly shifted upfield (189.0 ppm) in comparison to **2** (198.7 ppm). These data suggest that the coordination of PhN═NPh versus diphenylacetylene results in a much greater electron density at the palladium center corresponding to a higher degree of back-bonding. Complex **5** represents, to the best of our knowledge, the first NHC-Pd coordination complex of azobenzene.

Single crystal X-ray crystallography of complex **5** revealed a Y-shaped structure with a clear elongation of the N═N bond [1.412(6) Å] when compared to free PhN═NPh [1.25 Å] (Figure 1). The lengthening of the N═N bond is consistent with single bond character between the two nitrogen atoms. This feature is commonly observed among other transition metal-azobenzene complexes in a zero-oxidation state, including platinum [1.430(13) Å],[10] nickel [1.385(5) Å],[11] and iron [1.398(2) Å] analogues.[12] The Pd−$C_{carbenic}$ bond lengths in **5**

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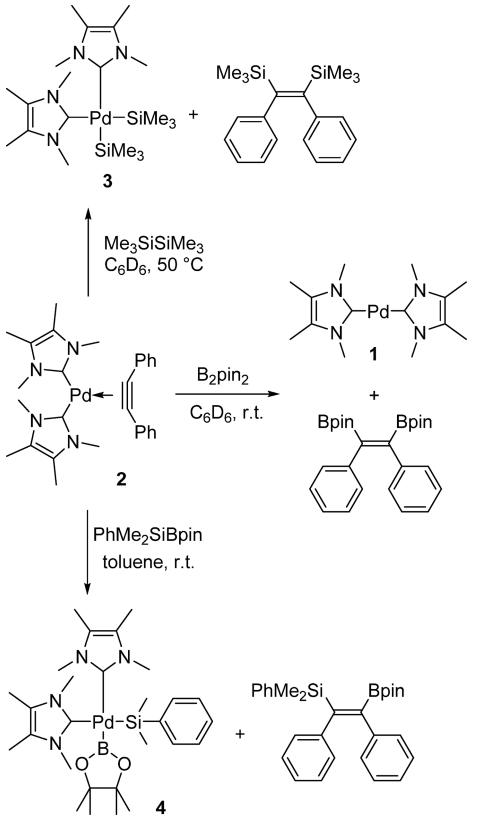
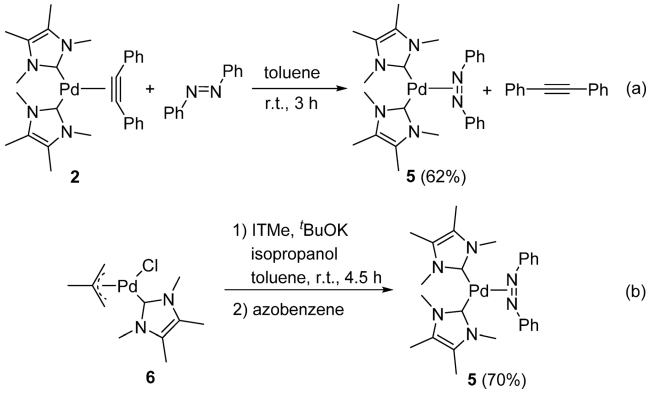
Organometallics 2018, 37, 1214−1218

Scheme 1. Additions of E−E′ Bonds to Alkynes Mediated by 2



Scheme 2. Two Routes for the Synthesis of Azobenzene Complex 5



are also longer [2.057(5) and 2.075(5) Å] than those in **2** [2.029(3) and 2.033(3) Å].

To further support our assignment of a zero-oxidation state to palladium, both **2** and **5** were subjected to cyclic voltammetry experiments. In both cases, an irreversible oxidation is observed (−0.660 V for **2**; −0.860 V for **5**) in a region consistent with previous reports for the oxidation of Pd(0).[13,14] In contrast, there is no evidence for the reverse process nor, indeed, reduction of Pd(II), which has been typically observed in the region −1.5 to −2.0 V for related systems.[13−18] Both complexes do exhibit an irreversible reduction at strongly cathodic potential (below −3.20 V) which we tentatively assign to the reduction of the parent [Pd(NHC)$_2$L] complex (L = alkyne or azobenzene),

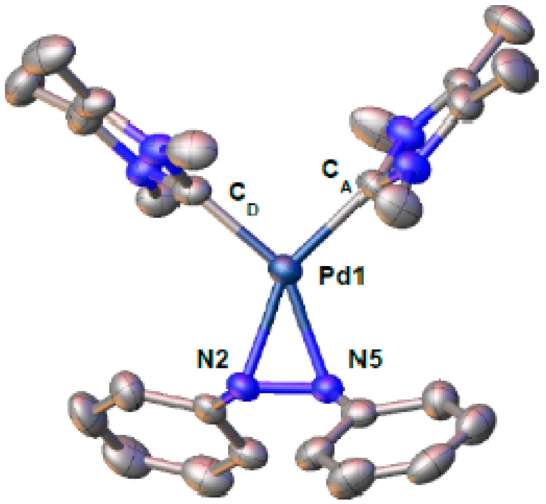


Figure 1. Solid state structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N2−N5: 1.412(5), Pd1−N2: 2.066(4), Pd1−N5: 2.093(4), Pd1−C_A: 2.075(5), Pd1−C_D: 2.057(5), N2−Pd1−N5: 39.69(17), C_A−Pd1−N5: 113.94(18), C_D−Pd1−N2: 110.4(2).

presumably in part associated with the NHCs. In the case of **5**, we noted an apparently reversible feature ($E_{1/2}$ −2.02 V), assignable to an essentially pure ligand-based process associated with azobenzene. This may reflect dissociation in THF solution, a process comparable to those observed for a range of free azobenzene derivatives (−1.7 to −1.98 V).[19]

Having recently reported the catalytic diboration and silaboration of azobenzenes using **2**, complex **5** was an ideal candidate on which to carry out stoichiometric reactions. Hence, the oxidative addition of silaboranes and disilanes to **5** afforded, as expected, the known hydrazine analogues **7** and **8**, respectively (Scheme 3).

To study further the capabilities of these (NHC)$_2$-Pd(0) complexes, we decided to explore analogous reactions with a digermane substrate. The palladium-catalyzed addition of Ge−Ge bonds to alkynes often requires relatively high palladium loadings, auxiliary ligands, or the use of activated or strained germanium species.[20] Platinum catalyzed processes are also documented.[21,22] To our delight, the oxidative addition of hexamethyldigermane to in situ prepared **2**, from complex **6**, at room temperature, led to the novel Pd(II) complex **9**, although we were unable to easily extract the digermylated alkene **10** (Scheme 4). However, a ^{1}H NMR experiment showed quantitative conversion of **2** to **10** after 3 days. Attempts to replicate this Ge−Ge reactivity on the azobenzene complex **5** invariably failed, even at higher temperature (100 °C).

Single crystals of **9** suitable for X-ray analysis were isolated from a saturated toluene solution at −30 °C. However, it was not possible to refine the data for lengthy discussions on bond lengths and angles (R_1 = 8.8% and wR_2 = 27.7%) apart from the molecular structure, displaying connectivity only and showing a *cis*-configuration (see the Supporting Information). Similarly, the solid-state structure of **10** was determined (see the Supporting Information).

Encouraged by these results, the catalytic reaction of $Me_3GeGeMe_3$ with diphenylacetylene was carried out, affording **10** in nearly quantitative yield (Scheme 5). This is an interesting reaction because germyl groups attached to sp^2 carbons can be readily transformed into iodides with retention

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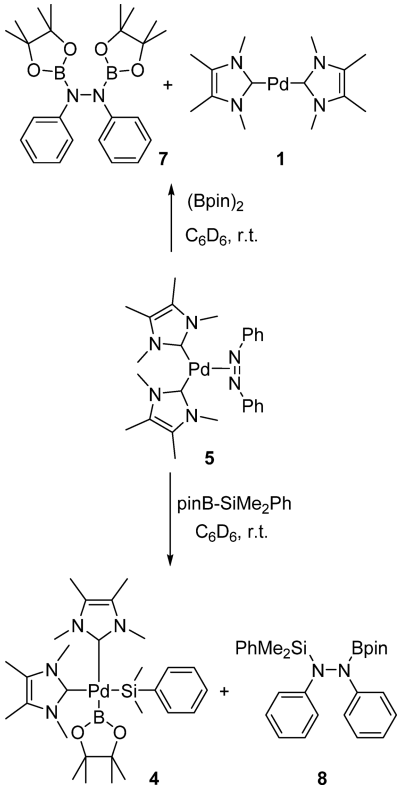
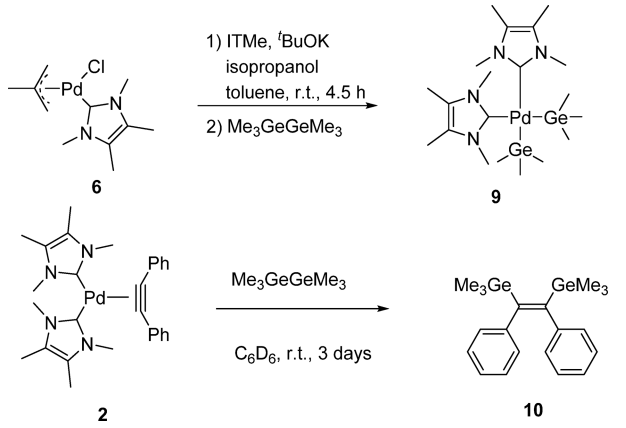
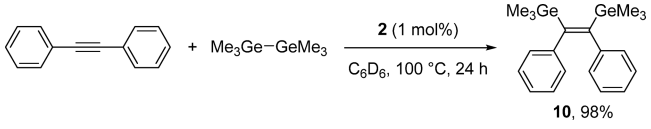
Scheme 3. Reactivity of Azobenzene Complex 5 with $(Bpin)_2$ and pinB-$SiMe_2Ph$



Scheme 4. Reactivity of Complex 2 with $(GeMe_3)_2$



Scheme 5. Catalytic Digermylation of Diphenylacetylene



of stereochemistry, allowing for the stereoselective synthesis of tetra-substituted alkenes.[23]

CONCLUSION

We have extended the chemistry of the low-buried volume complexes **1** and **2** to include the isolation of the novel azobenzene complex **5**, which was shown to react with E–E′ bonds (B–Si and B–B) to afford substituted hydrazines. Hexamethyldigermane undergoes oxidative addition to **2** to afford Pd(II) complex **9** and adds stereoselectively to diphenylacetylene using catalytic amounts of **2**. These findings underline again the excellent potential of the low-buried volume complexes **1** and **2** in the catalytic activation of E–E′ bonds. We are actively investigating further applications of these complexes in the synthesis of high value end products.

EXPERIMENTAL SECTION

The manipulation of air-sensitive compounds and their spectroscopic measurements were undertaken using standard Schlenk line techniques under predried Ar (using a BASF R3-11(G) catalyst and 4 Å molecular sieves), or in a MBraun glovebox under N_2 (O_2 < 10.0 ppm). All glassware was dried in a 160 °C oven prior to use. Celite was predried in a 200 °C oven and then dried with a heat gun under a dynamic vacuum prior to use. Filter cannulae equipped with microfiber filters were dried in an oven at 160 °C prior to use. Solvents employed in air-sensitive reactions were dried using vacuum distillation, followed by distillation over potassium, e.g., hexane, toluene, or stored over activated 4 Å molecular sieves under an Ar atmosphere (e.g., 2-methyl tetrahydrofuran). Dried solvents were degassed and stored over Ar in ampules containing activated molecular sieves. For reactions carried out under ambient conditions, solvents were used as purchased. Deuterated benzene, C_6D_6, was degassed and dried by refluxing over potassium for 3 days, vacuum transferred into ampules, and stored under N_2. Deuterated chloroform, $CDCl_3$, was used as purchased. NMR spectra were recorded on a Varian VNMRS 400 (^{1}H 399.5 MHz; ^{13}C{^{1}H}n 100.5 MHz; ^{11}B{^{1}H} 128.2 MHz; ^{19}F 375.9 MHz; ^{29}Si{^{1}H} 79.4 MHz) or 500 (^{1}H 499.9 MHz; ^{13}C{^{1}H} 125.7 MHz). Chemical shifts are reported in ppm. The spectra were referenced to the corresponding protic solvent (^{1}H) or signals of the solvent (^{13}C). ^{11}B{^{1}H}, ^{19}F, and ^{29}Si{^{1}H} NMR spectra were referenced externally relative to $BF_3{\cdot}OEt_2$, $CFCl_3$ (10%), and $SiMe_4$ respectively.

Single crystal X-ray diffraction data were collected at the University of Sussex on an Agilent Technologies Xcalibur Gemini Ultra diffractometer (λCu(Kα) = 1.54184 or λMo(Kα) = 0.71073) equipped with an Eos CCD area detector. Data were collected at 173 K using an Oxford Cryosystems Cobra low temperature device. Data were processed using CrysAlisPro, and the unit cell parameters were refined against all data. Semiempirical absorption corrections were carried out using the MULTI-SCAN program.[24] The structures were solved by using an intrinsic phasing method (SHELXT),[25] and refined F0 by full matrix least-squares refinement using −2013,[26] within OLEX2.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added at calculated positions and refined using riding models with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atoms. The crystal data of **5** were collected on a BRUKER X8-APEC II diffractometer with a CCD area detector and multilayer mirror monochromated Mo(Kα) radiation. The structure was solved using an intrinsic phasing method (SHELXT),[25] refined with the SHELXL program,[28] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

The following structures have been assigned CCDC numbers (CCDCs 1824672, **5**; 1824670, **9**; 1824671, **10**).

[Pd(ITMe)$_2$(PhN═NPh)] (5). Complex **2** (0.032 g, 0.06 mmol) and PhN═NPh (0.019 g, 0.10 mmol) were dissolved in toluene (5.0 mL). The resulting mixture was stirred at room temperature for 3 h. At this stage, the volatiles were removed in vacuo and the crude material was washed and recrystallized in a toluene/hexane solution (3:1, 2 × 2.0 mL). The resulting yellow powder was washed with pentane (3 × 2.0 mL). Yield: 0.020 g (62%). ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.80 (m, 4H, Ph), 7.26 (m, 4H, Ph), 6.87 (pseudo-t, J = 7.2 Hz, 2H, p-Ph), 3.31 (s, 12H, N(1,3)-CH_3), 1.38 (s, 12H, C(4,5)-CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 189.0 (NCN), 163.0 (i-Ph), 128.9

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Organometallics 2018, 37, 1214−1218

(Ph), 124.1 (C(4,5)-CH_3), 120.5 (Ph), 117.0 (p-Ph), 35.2 (N(1,3)-CH_3), 8.7 (C(4,5)-CH_3) Elem. Anal. Calcd for $C_{26}H_{34}N_6Pd$: C, 58.15%; H, 6.38%; N, 15.65%. Found: C, 58.10%; H, 6.47%; N, 15.60%.

Scale-Up Synthesis of 5. Isopropanol (12.2 μL, 0.16 mmol) was added to a stirred mixture of [(ITMe)Pd(methallyl)Cl] (**6**) (0.051 g, 0.16 mmol), ITMe (0.024 g, 0.19 mmol), and potassium *tert*-butoxide (0.019 g, 0.17 mmol) suspended in toluene (5.0 mL). The reaction mixture was stirred at room temperature under a N_2 atmosphere for 4.5 h, at which point PhN═NPh (0.036 g, 0.20 mmol) was added and the solution was stirred for 17 h at room temperature. The resulting reaction mixture was filtered, the filtrate's volatiles were removed in vacuo, and the crude material was recrystallized in a toluene/hexane solution (2:1, 2 × 15.0 mL) at −35 °C. A yellow solid was obtained after filtration and subsequently washed with hexane (3 × 5.0 mL). Yield: 0.060 g (70%).

Synthesis of *cis*-[Pd(ITMe)$_2$(GeMe$_3$)$_2$] (9). Isopropanol (10.0 μL, 0.14 mmol) was added to a suspension of [(ITMe)Pd(methallyl)Cl] (**6**) (0.046 g, 0.14 mmol), ITMe (0.019 g, 0.16 mmol), and potassium *tert*-butoxide (0.017 g, 0.15 mmol) in toluene (10.0 mL). The resulting reaction mixture was stirred at room temperature under a N_2 atmosphere for 4.5 h. At this stage, $(GeMe_3)_2$ (58.0 μL, 0.29 mmol) was added and the reaction mixture was stirred for 19 h at room temperature. The solution was then filtered via cannula, the filtrate's volatiles were removed in vacuo, and the resulting off-white solid was washed with hexane (3 × 5.0 mL). Yield: 0.050 g (59%). ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 3.33 (s, 12H, N(1,3)-CH_3), 1.42 (s, 12H, C(4,5)-CH_3), 0.64 (s, 18H, $GeMe_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ_C = 193.6 (NCN), 123.5 (C(4,5)-CH_3), 35.0 (N(1,3)-CH_3), 8.6 (C(4,5)-CH_3), 7.6 ($GeMe_3$). Elem. Anal. Calcd for $C_{20}H_{42}N_4Ge_2Pd$: C, 40.70%; H, 7.17%; N, 9.49%. Found: C, 41.13%; H, 7.44%; N, 9.46%

Synthesis of (*Z*)-1,2-Diphenyl-1,2-bis(trimethylgermyl)-ethane (10). In a glovebox, a Young's tap NMR tube was loaded with complex **2** (0.004 g, 8.23 μmol), $(GeMe_3)_2$ (0.005 g, 22.93 μmol), and C_6D_6 (0.7 mL). The progress of the reaction was monitored by ^{1}H NMR spectroscopy, showing full conversion to **10** after stirring at room temperature for 3 days.

Catalytic Synthesis of 10. Diphenylacetylene (0.025 g, 0.14 mmol), $(GeMe_3)_2$ (45.0 μL, 0.22 mmol), and **2** (0.75 mg, 1.41 μmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was heated under a N_2 atmosphere to 100 °C for 24 h. Upon cooling, the volatiles were removed in vacuo, and the crude material was redissolved in CH_2Cl_2 (10.0 mL) and subsequently filtered through flame-dried Celite. The filtrate volatiles were removed in vacuo to reveal an off-white solid. Yield 0.057 g (98%). ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 6.99 (m, 4H, Ph), 6.87 (m, 2H, p-Ph), 6.66 (m, 4H, Ph), 0.24 (s, 18H, $GeMe_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ_C = 157.2 (C═C), 146.1 (i-Ph), 127.7 (Ph), 127.3 (Ph), 124.4 (p-Ph), 1.5 [$GeMe_3$]. Elem. Anal. Calcd for $C_{20}H_{28}Ge_2$: C, 58.06%; H, 6.82%; Found: C, 58.07%; H, 6.89%;

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00112.

Scanned ^{1}H and ^{13}C NMR spectra for all compounds synthesized herein (PDF)

Accession Codes

CCDC 1824670−1824672 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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